

WHAT IS CLAIMED IS:

1. A process of forming a HA/ZrO₂ complex coating on a Co-Cr-Mo alloy substrate, the Co-Cr-Mo substrate being subject to an electrolytic deposition sequentially in a ZrO(NO₃)₂ bath and a mixed solution of Ca(NO₃)₂.4H₂O and NH₄H₂PO₄, and then the substrate being sintered to form the HA/ZrO₂ complex coating on the Co-Cr-Mo substrate.
2. The process of claim 1, wherein the electrolytic deposition of the Co-Cr-Mo substrate in the ZrO(NO₃)₂ bath forms a Zr(OH)₄ colloidal layer on the Co-Cr-Mo substrate.
- 10 3. The process of claim 1, wherein the electrolytic deposition of the Co-Cr-Mo substrate in the mixed solution of Ca(NO₃)₂.4H₂O and NH₄H₂PO₄ forms a Ca₁₀(PO₄)₆(OH)₂ layer on the Zr(OH)₄ colloidal layer.
4. The process of claim 1, wherein the substrate having the Ca₁₀(PO₄)₆(OH)₂ layer and the Zr(OH)₄ colloidal layer thereon is dried and sintered to form the HA/ZrO₂ complex coating.
- 15 5. The process of claim 1, wherein the concentration of the ZrO(NO₃)₂ bath is the range of 0.0001M ~ 0.5M.
6. The process of claim 1, wherein the concentration of the ZrO(NO₃)₂ bath is the range of 0.001M ~ 0.02M.
- 20 7. The process of claim 1, wherein the duration of electrolytic depositing the substrate in the ZrO(NO₃)₂ bath is about 150s ~ about 3500s.
8. The process of claim 1, wherein the duration of electrolytic depositing the substrate in the ZrO(NO₃)₂ bath is about 300s ~ about 2000s.

9. The process of claim 1, wherein the concentrations of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $\text{NH}_4\text{H}_2\text{PO}_4$ in the mixed solution are respectively $0.02\text{M} \sim 0.15\text{M}$ 及 $0.005\text{M} \sim 0.5\text{M}$ 。

10. The process of claim 1, wherein the concentrations of the $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $\text{NH}_4\text{H}_2\text{PO}_4$ in the mixed solution are respectively $0.04\text{M} \sim 0.1\text{M}$ and $0.02\text{M} \sim 0.25\text{M}$.

11. The process of claim 1, wherein the duration of electrolytic depositing the substrate in the mixed solution of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $\text{NH}_4\text{H}_2\text{PO}_4$ is about $100\text{s} \sim 3000\text{s}$.

12. The process of claim 1, wherein the duration of electrolytic depositing the substrate in the mixed solution of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $\text{NH}_4\text{H}_2\text{PO}_4$ is about $500\text{s} \sim 2000\text{s}$.

13. The process of claim 1, wherein voltage used for electrolytic depositing the substrate in the $\text{ZrO}(\text{NO}_3)_2$ bath is about $-0.6\text{ V} \sim -2.5\text{ V}$.

14. The process of claim 1, wherein voltage used for electrolytic depositing the substrate in the $\text{ZrO}(\text{NO}_3)_2$ bath is about $-0.75\text{ V} \sim -1.1\text{ V}$.

15. The process of claim 1, wherein voltage used for electrolytic depositing the substrate in the mixed solution of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $\text{NH}_4\text{H}_2\text{PO}_4$ is about $-0.5\text{ V} \sim -3\text{ V}$.

16. The process of claim 1, wherein voltage used for electrolytic depositing the substrate in the mixed solution of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $\text{NH}_4\text{H}_2\text{PO}_4$ is about $-0.6\text{ V} \sim -1.4\text{ V}$.

17. The process of claim 1, wherein the substrate having the $\text{Zr}(\text{OH})_4$ colloidal layer and the $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ layer thereon is slowly dried at constant temperature and humidity before sintered.

18. The process of claim 1, wherein the substrate is further dried at temperature of about 15 ~ 40°C and relative humidity of more than 75% before sintered.

19. The process of claim 1, wherein the sintering temperature is not higher than 500°C.

5 20. The process of claim 1, wherein the sintering temperature is raised at stages, the temperature changing rate is not quick, and the temperature is kept for a while between two temperature changing stages.

21. The process of claim 20, wherein the temperature is raised at 2°C/min at each temperature changing stage.

10 22. A process of forming a HA/ZrO₂ complex coating on a Co-Cr-Mo alloy substrate, the Co-Cr-Mo substrate being subjected to an electrolytic deposition sequentially in a ZrO(NO₃)₂ bath and a mixed solution of Ca(NO₃)₂.4H₂O and NH₄H₂PO₄, then the substrate being slowly dried, and the substrate being sintered at a temperature not higher than 500°C to form the HA/ZrO₂ complex coating on the
15 Co-Cr-Mo substrate, wherein the sintering temperature is raised at several temperature stages.

23. The process of claim 22, wherein the electrolytic deposition of the Co-Cr-Mo substrate in the ZrO(NO₃)₂ bath forms a Zr(OH)₄ colloidal layer on the Co-Cr-Mo substrate.

20 24. The process of claim 22, wherein the electrolytic deposition of the Co-Cr-Mo substrate in the mixed solution of Ca(NO₃)₂.4H₂O and NH₄H₂PO₄ forms a Ca₁₀(PO₄)₆(OH)₂ layer on the Zr(OH)₄ colloidal layer.

25. The process of claim 22, wherein the substrate having the $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ layer and the $\text{Zr}(\text{OH})_4$ colloidal layer thereon is dried and sintered to form the HA/ZrO₂ complex coating.

26. The process of claim 22, wherein the concentration of the $\text{ZrO}(\text{NO}_3)_2$ bath is
5 the range of 0.0001M ~ 0.5M.

27. The process of claim 22, wherein the concentration of the $\text{ZrO}(\text{NO}_3)_2$ bath is
the range of 0.001M ~ 0.02M.

28. The process of claim 22, wherein the duration of electrolytic depositing the
substrate in the $\text{ZrO}(\text{NO}_3)_2$ bath is about 150s ~ about 3500s.

10 29. The process of claim 22, wherein the duration of electrolytic depositing the
substrate in the $\text{ZrO}(\text{NO}_3)_2$ bath is about 300s ~ about 2000s.

30. The process of claim 22, wherein the concentrations of the $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$
and $\text{NH}_4\text{H}_2\text{PO}_4$ in the mixed solution are respectively 0.02M ~ 0.15M 及 0.005M ~
0.5M。

15 31. The process of claim 22, wherein the concentrations of the $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$
and $\text{NH}_4\text{H}_2\text{PO}_4$ in the mixed solution are respectively 0.04M ~ 0.1M and 0.02M ~
0.25M.

20 32. The process of claim 22, wherein the duration of electrolytic depositing the
substrate in the mixed solution of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $\text{NH}_4\text{H}_2\text{PO}_4$ is about 100s ~
3000s.

33. The process of claim 22, wherein the duration of electrolytic depositing the
substrate in the mixed solution of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $\text{NH}_4\text{H}_2\text{PO}_4$ is about 500s ~
2000s.

34. The process of claim 22, wherein voltage used for electrolytic depositing the substrate in the ZrO(NO₃)₂ bath is about -0.6 V ~ -2.5 V.

35. The process of claim 22, wherein voltage used for electrolytic depositing the substrate in the ZrO(NO₃)₂ bath is about -0.75 V ~ -1.1 V.

5 36. The process of claim 22, wherein voltage used for electrolytic depositing the substrate in the mixed solution of Ca(NO₃)₂.4H₂O and NH₄H₂PO₄ is about -0.5 V ~ -3V.

37. The process of claim 22, wherein voltage used for electrolytic depositing the substrate in the mixed solution of Ca(NO₃)₂.4H₂O and NH₄H₂PO₄ is about -0.6 V ~ -0.4 V.

10 38. The process of claim 22, wherein the substrate having the Zr(OH)₄ colloidal layer and the Ca₁₀(PO₄)₆(OH)₂ layer thereon is slowly dried at constant temperature and humidity before sintered.

39. The process of claim 22, wherein the substrate is further dried at temperature 15 of about 15 ~ 40°C and relative humidity of more than 75% before sintered.